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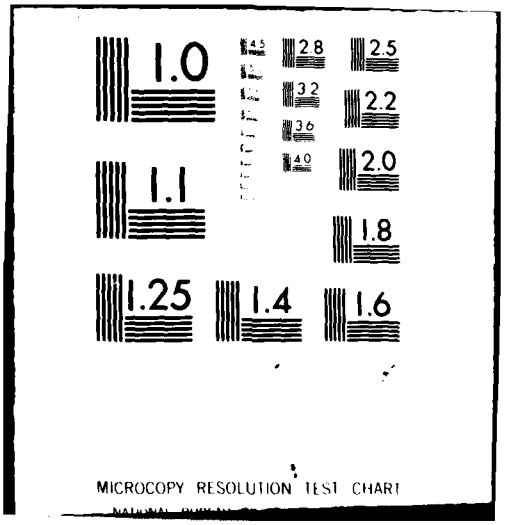
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Semi-Annual Report

to

OFFICE OF NAVAL RESEARCH

on

THE STUDY OF ATOM-ATOM, ELECTRON-MOLECULE AND PHOTON MOLECULE PROCESSES

July 1, 1973-June 30, 1974

Contract No. N00014-67-A-0126-0017
N00014-75-C-0498

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October 15, 1974

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I. INTRODUCTION

The funding on this contract was initiated in February 1, 1972. Thus the period of July 1, 1973-June 30, 1974, is the second full year of research activity. The personnel working on the research projects covered under this contract are Dr. E. J. Shipsey, Research Associate (twelve months), Mr. P. L. DeVries and the principal investigator. The 1973-74 year was a successful one in terms of publications, with five papers representing work sponsored by this contract appearing in the journals and five others accepted for publication (see Section IV). The close working relationship established with the experimental and scattering analysis atom-atom collision group at Stanford Research Institute (SRI) has continued. This enterprise has produced two papers which have been published, two more papers which have been accepted for publication in Physical Review, and three other manuscripts based on this collaborative enterprise are in progress. This will be reviewed in somewhat more detail in Section II. Further principal efforts in this research have been the study of photon processes and in particular multiphoton processes for the hydrogen molecules and theoretical studies of chemical reactions.

II. ATOM-ATOM SCATTERING

The focus of the atom-atom scattering work has been two-fold. The problem which has received most attention is application of the existing computer codes for the development of molecular wave functions and the computation of transition matrix elements to provide an adiabatic basis set for collision cross-section computations. The second activity is an effort to improve the effectiveness, the accuracy and the reliability of the available procedures for computation of the matrix elements between the adiabatic states.

A. Scattering Processes Involving Helium Atoms

Two processes involving the collision of helium atoms have been investigated. The differential and total cross-sections for the excitation reactions

$$He(1^1S)+He(1^1S) \rightarrow He(1^1S)+He(2^1P)$$

$$\rightarrow He(1^1S)+He(2^1S)$$

in the range of 50 to 250 eV_{cm} have been computed. The calculated differential cross-sections compare well with the experimental data of Morganstein, Barat and Lorents [1]. Additionally, it is determined that the primary product in the excitation to the N=2 level is the production of $He(2^1P)$. The total cross-sections for production of $He(2^1S)$ are approximately 10% of the magnitude of those for $He(2^1P)$ at energies above 100 eV.

The differential and total cross-sections have also been computed for the excitation exchange process

$$He(2^1S)+He(1^1S) \rightleftarrows He(2^1P)+He(1^1S)$$

for energies less than 100 eV_{cm}. The inelastic differential cross-sections are forwardly peaked with most of the scattering appearing at reduced angles $\tau=E\theta\leq 250$ eV-degrees. The total elastic cross-section for the excitation to

$He(2^1P)$ by $He(1^1S)$ was found to be greater than $1x10^{-17}$ cm^2 at thermal energies and yields a Boltzmann averaged rate of $k(300°K)=2.9x10^{-12}$ cm^3/sec. This compares well with the experimental value of $1.8x10^{-12}$ cm^3/sec of Payne, Hurst and Klots [2]. Sharp orbiting resonances are found in the inelastic total cross-sections at energies below 3 eV. The total excitation cross-section was found to rise rapidly from threshold (0.60 eV) to values greater than $1x10^{-16}$ cm^2 at collision energies above 4 eV.

A number of experiments are suggested by these computations. For example, it should be possible to observe the sharp low energy orbiting resonances in a scattering experiment by laser-pumping a monoenergetic beam of $He(2^1S)$ metastables to the $He(2^1P)$ state, colliding the resulting beam with ground state helium atoms and then monitoring the radiation emitted by the decaying $He(2^1P)$ beam.

B. B^{+3}+He Collisions

Computations have been made on the potential curves and coupling matrix element belonging to the lowest two Σ states. An increasingly complex sequence of wave functions was investigated. This has been found to account for the lowest energy results of Zwalley and Cable [3]. Minimal basis calculations were carried out for the Π-Σ coupling. The later coupling appears to be important at higher energies.

C. CsH^+ Reactions

There have been a number of experimental studies of low energy charge transfer processes of protons on Cs atoms. The process is of theoretical interest because effects occur at very large internuclear separations. We have established a one-electron model and computed potential curves for the second- and third-lowest Σ states and the lowest Π state. The coupling element between

the two Σ states has been computed as well as the coupling element between the Π state and the third-lowest Σ state.

D. Computation of Σ-Σ Coupling

An excellent computer code for the Σ-Σ coupling elements was implemented by Larry L. Lenamon [4] and employed for a one-electron problem. This has now been debugged for many electron systems, and some numerical aspects improved. Questions of basis size and mesh spacing have been explored.

III. PHOTON PROCESSES

There are four basic results obtained by this research program in the area of photon processes. Three of these represent applications of theory to interesting cases, and the fourth is a set of extensions of the theoretical analyses for the use of sum rule computation in the study of single and multi-photon processes.

A. Transition Matrix Elements for He

We have obtained the most accurate set of transition matrix elements and oscillator strengths yet obtained for transition

$$He_2(A\,^1\Sigma_u^+) \rightarrow He_2(X\,^1\Sigma_g^+)+h\nu \ .$$

These computations resolved the discrepancy between the length and velocity forms of the matrix elements in the previous calculations of Allison, Browne and Dalgarno [5].

B. Matrix Element Bounds

Evaluation has been made of the usefulness of the Weinhold [6] bounds for polarizability on the context of the H_2 molecule. The bracketing of polarizabilities over a range of internuclear separations for the H_2 molecule appear to be within 1% on each side. This is an extremely tight bound and strongly suggests the value of application of the Weinhold bounds in the computation of polarizabilities.

C. Analysis of Finite Sum Rules

In order to pursue the computation of the multi-photon processes by sum rule methods, it was necessary to develop extensions of existing sum rule analyses. Two significant extensions were developed. Papers on this work are in preparation.

(1) It was established that the set of sum rules discussed by Epstein and Dalgarno [7] can be satisfied without requiring the initial state to be an exact state or even that the Hamiltonian matrix be diagonalized on the extended basis. It is only the equivalence of the length and velocity formulations of the transition matrix element which require the initial state to be an exact state or that H be diagonalized in the extended basis. This refinement of the finite sum rule analysis removes one uncertainty from the application of this analysis.

(2) It was also necessary to extend the Dalgarno-Epstein theorems to cover application to properties which are not diagonal in the electronic wave function. This has been accomplished, and the results are detailed in the Ph.D. dissertation of P. L. DeVries [8].

D. Two-Photon Processes

The computation of the two-photon excitation

$$H_2(X^1\Sigma_g^+) \xrightarrow[h\nu_1+h\nu_2]{} H_2(E,F^1\Sigma_g^+)$$

has been carried out in detail. The transition probabilities for the two-photon process are found to be rather high. For example, a photon flux of 9.9×10^{-19} cm^2/sec gives a cross-section of 8.5×10^{-22} cm^4/sec. The detailed analysis is given in the Ph.D. dissertation of P. L. DeVries [8], and preparation of a manuscript for publication is in progress..

IV. CHEMICAL REACTION PROCESSES

The work described here represents a continuing research program in theoretical analyses of chemical reactions. One paper on this subject appeared in the Journal of Chemical Physics during the contract period, and another has been accepted for publication. The published paper (Section VI.A.) shows how unitary approximations of the scattering matrix may be constructed by means of the theory introduced earlier. No specific approximations were proposed. However, the mathematical framework is established into which approximations may be inserted. The paper (Section VI.B.) which has been accepted for publication analyzes the semi-classical approximations and offers remedies for some of its problems. The subdynamic collision theory replaces the second-order coupled differential equation by a first-order system (with an anti-Hermitian coupling matrix element which gives a unitary solution). This, of course, involves another differential equation. For the first time here a formal, exact anti-Hermitian coupling matrix is given which asympotically approaches the semi-classical expression. The validity of the semi-classical expression is analyzed numerically for a simple example. The results show the semi-classical expression works well away from a turning point but fails very close to the turning point. It is also shown that the semi-classical expression is an approximation to the perturbation theory result and that the perturbation theory is capable of making up for the deficiencies of the semi-classical theory (in the example investigated). The perturbation theory extends the coupling matrix elements through the turning points.

V. OTHER WORK

Two other papers relating to work completed some years ago were written up and have been accepted for publication in the Journal of Chemical Physics.

These papers (Section VI.B.) deal primarily with adiabatic corrections to the molecular potential curves defined by the fixed nuclei electronic hamiltonian.

VI. CONTRACT-RELATED PUBLICATIONS

A. Published Papers. Reprints or Xeroxes Attached

1. "Theoretical Low Energy Inelastic-Scattering Cross-Section for $He(2^3S)+He(1^1S) \rightarrow He(2^3P)+He(1^1S)$: Curve Crossing Between the $c^3\Sigma_g^+$ and $b\ ^3\Pi_g$ States of He_2", Phys. Rev. A. 8, 2372 (1973), L. Lenamon, J. C. Browne and R. E. Olson.

2. "Low-Energy Inelastic Scattering of $He(2^3S)$ on $He(1^1S)$", Phys. Rev. A. 8, 2380 (1973), R. E. Olson, R. Morgenstein, D. C. Lorents, J. C. Browne and L. Lenamon.

3. "Comparison of Quantum Mechanical and Transition State Theory Reaction Probabilities for the Reaction O+HBr→OH+Br. A Reply.", J. Chem. Phys. 59, 2170 (1973), E. J. Shipsey.

4. "In-out Decomposition for Inelastic Collisions as Subdynamics", J. Chem. Phys. 59, 5109 (1973), E. J. Shipsey.

5. "In-out Decomposition for Inelastic Collisions as Subdynamics. II. Scattering Matrix and Approximation Methods", J. Chem. Phys. 60, 1589 (1974), E. J. Shipsey.

B. Papers Accepted for Publication

1. "Theoretical Low Energy Scattering Cross-Sections for $He(2^1S)+He(1^1S) \rightleftarrows He(2^1P)+He(1^1S)$" (to appear in Phys. Rev. A.), E. J. Shipsey, J. C. Browne and R. E. Olson.

2. "Theoretical Cross-Sections for $He(1^1S)+He(1^1S) \rightarrow He(1^1S)+He(2^1P)$ and $He(2^1S)$" (to appear in J. Phys. B: Atom. Molec. Phys.), R. E. Olson, E. J. Shipsey and J. C. Browne.

3. "In-out Decomposition for Inelastic Collisions as Subdynamics. III. Perturbation Theory and the Semi-classical Limit" (to appear in J. Chem. Phys.), E. J. Shipsey.

4. "Adiabatic Ab Initio Potential Curves for the $B'^1\Sigma_u^+$ State of H_2" (to appear in J. Chem. Phys.), A. L. Ford, J. C. Browne, P. L. DeVries and E. J. Shipsey.

5. "The Computation of Nuclear Motion and Mass Polarization Energy Corrections for Several States of the Hydrogen Molecule" (to appear in J. Chem. Phys.), A. L. Ford, E. M. Greenawalt and J. C. Browne.

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8. P. L. DeVries, Ph.D. Dissertation, Department of Physics, The University of Texas at Austin, August, 1974.